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(54) Title: ELECTROPHORETIC DISPLAYS CONTAINING MODIFIED PARTICLES

(57) Abstract: An electrophoretic display containing modified particles is described. As well as non-emissive display systems. In the electrophoretic display, an arrangement of microscopic containers is used, wherein each container contains a dielectric fluid and a suspension of particles having attached at least one organic group, wherein the organic group includes at least one ionic group, ionizable group, or both, and wherein fluid and the particles contrast visually. The electrophoretic display also includes first and second electrodes wherein the arrangement is located between these electrodes and wherein one of the electrodes is substantially visually transparent. The electrophoretic display further includes means for creating a potential difference between the two electrodes so that the potential difference causes the particles to migrate toward one of the electrodes.



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**ELECTROPHORETIC DISPLAYS CONTAINING MODIFIED PARTICLES****BACKGROUND OF THE INVENTION**

The present invention relates to electrophoretic displays and non-emissive display systems. The present invention, more particularly, relates to electrophoretic displays and non-emissive display systems, using particles, such as pigments, which improve the display.

U.S. Patent Nos. 5,961,804 and 5,930,026, for instance, describe electrophoretic displays using microcapsules which contain a suspension of particles in a dielectric fluid. Through the use of two electrodes which are located on opposite sides of the microcapsule arrangement, a potential difference can cause the particles to migrate toward one of the electrodes thus forming a display which can be used to form images or text on a display which is located on one of the electrodes since one of the electrodes is transparent. The electrophoretic displays form images and text through the use of a potential difference between two electrodes and a quantity of charged particles. If these charged particles agglomerate they would not remain suspended in the dielectric fluid, and the ability to form reusable display of images or text can be greatly diminished if not made problematic. Accordingly, there is a need to improve upon the electrophoretic display technology in order to ensure that clear and visually sharp images can be obtained using electrophoretic display technology and pigment particles.

**SUMMARY OF THE PRESENT INVENTION**

A feature of the present invention is to provide electrophoretic displays which provide sharp and clear images on the display.

Another feature of the present invention is to provide an electrophoretic display wherein the suspension of charged particles is maintained and agglomeration of the charged particles is significantly reduced, if not, eliminated.

Another feature of the present invention is to provide non-emissive display systems which accomplish the above-described benefits.

Additional features and advantages of the present invention will be set forth in part in the description that follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and attained by means of the elements and combinations particularly pointed out in the description and appended claims.

To achieve these and other advantages, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention relates to an electrophoretic display having an arrangement of microscopic containers and first and second electrodes disposed on and covering opposite sides of the arrangement. One of the electrodes is substantially visually transparent. The electrophoretic display also has means for creating a potential difference between the two electrodes. Also, each microscopic container in the electrophoretic display has at least one type of dielectric fluid and a suspension of particles in the dielectric fluid. The fluid and the particles are contrasting visually. The particles for purposes of the present invention have attached at least one organic group, wherein the organic group contains an ionic and/or ionizable group and wherein the organic group on the particles causes the particles to migrate towards one of the electrodes when there is a potential difference created between the two electrodes.

The present invention further relates to a non-emissive display system which contains a pair of oppositely disposed electrodes and at least one display element located between the electrodes. The display element is visually responsive to a potential difference between the two electrodes. The non-emissive display system further has a display piezoelectric element connected to the electrodes wherein deformation of the piezoelectric element produces the potential difference. The display element in the non-emissive display system contains a substantially two-dimensional arrangement of discrete microscopic containers as described above for the electrophoretic display. The particles within the container, as stated above, have attached at least one organic group wherein the organic group contains an ionic and/or ionizable group such that the potential difference occurring between the two electrodes causes these particles to migrate toward one of the electrodes.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide a further explanation of the present invention, as claimed.

#### **DETAILED DESCRIPTION OF THE PRESENT INVENTION**

The present invention relates to an electrophoretic display and a non-emissive display system. The electrophoretic display contains an arrangement of microscopic containers which are preferably discrete. The microscopic containers each contain a dielectric fluid and particles which are suspended in the dielectric fluid. The fluid and the particles contrast

visually so as to have different colors. The particles for purposes of the present invention have attached at least one organic group, wherein the organic group includes an ionic and/or ionizable group. A first and second electrodes are located on opposite sides of the arrangement of microscopic containers and cover this arrangement on both sides. At least one of the electrodes is substantially visually transparent. Also, the electrophoretic display of the present invention includes means for creating a potential difference between the two electrodes such that when there is a potential difference, the particles migrate toward one of the electrodes. By permitting the migration of particles in various containers to one of the electrodes, images including text can be created at the electrode which is visually transparent.

The present invention further relates to a non-emissive display system which contains an arrangement of discrete microscopic containers as described above which contains the dielectric fluid and the particles suspended within the fluid. These elements comprise the display element. The non-emissive display system further includes at least two electrodes wherein the display element is located between the two electrodes and the display element is visually responsive to a potential difference between the electrodes. Further, the non-emissive display system contains a display piezoelectric element connected to the electrodes wherein deformation of the piezoelectric element produces a potential difference which causes the particles to migrate toward one of the electrodes.

Another embodiment of the present invention relates to a rewritable display media in which an optical response results from the movement of particles in an electric field, wherein the particles have attached at least one organic group having at least one ionic group or ionizable group or both.

The electrode for purposes of the present invention can be any conventional electrode which satisfies the needs of the electrophoretic display. For instance, the electrode can be a semiconductor which is located on a substrate such as glass, mylar, and the like. Such electrodes as described in U.S. Patent Nos. 3,668,106 and 4,305,807 can be used for purposes of the present invention.

A driver circuit, for instance, can be electrically connected to the electrodes which is capable of creating a potential difference between the electrodes to cause migration of the particles to one or to the other electrode within the desired switching time.

With respect to the microscopic containers, as indicated above, these containers each contain a dielectric fluid and particles which are suspended within the dielectric fluid. The

microscopic containers or microcapsules can be any shape, spherical or non-spherical but are preferably spherical or of a similar round shape. The dimensions can vary and are preferably from about 5 to about 500 microns, and more preferably from about 25 to 250 microns. The walls of the microscopic containers preferably exhibit resistivity to the dielectric fluid.

5           The dielectric fluid or liquid can be any dielectric fluid as long as it is compatible with the particles present in the container. Preferably, the dielectric fluid is a hydrophobic liquid. The hydrophobic liquid is generally chosen based on viscosity, dielectric constant, charge, and density. Dielectric fluids that can be used, include, but are not limited to, darkly colored hydrophobic fluids, such as isoparaffinic petroleum solvent or  
10   trichlorotrifluoroethane, or mixtures thereof. Also, halogenated hydrocarbons can also be used and the dielectric liquid can also include dyes or other coloring agents (e.g., electrically neutral pigments) to create the desired color of the dielectric fluid.

          The dielectric fluid can also be, for purposes of the present invention, an electrophoretic fluid which may include one or more fluids.

15           For purposes of the present invention, the particles are particles having at least one organic group attached to the particles. Preferably, the particle is a pigment particle. The pigment can be any wide range of colors. The particles can be any size such as from about 100 microns or more to less than one micron and preferably have a size range of from about 0.05 microns to about 25 microns.

20           The displays of the present invention comprise particles having an attached organic group. The choice of organic groups is dependent on both the dielectric fluid and the capsule material. The organic group should enable the particles to be dispersible in the dielectric fluid but not interact with the capsule. Thus, the choice of organic group as well as the amount attached must be made carefully in order for the display to function properly.

25           In previous attempts to make electrophoretic displays, the particles were treated or coated with charge-control agents which may have been adsorb directly onto the particle. The present invention, on the other hand, attaches at least one type of organic group on the particles, wherein this attachment is preferably a chemical attachment or covalent bond. Such an attachment provides great stability to the organic group remaining with the particle and  
30   not becoming disassociated in the dielectric liquid. A major fall back of previous electrophoretic displays is the lack of ability to maintain a consistent charge or chargeable particle due to the instability of the charge-control agent being merely coated or adsorbed

onto the particle. After all, if the charge-control agent is susceptible to being removed from the particle, the electrophoretic display will operate at less than optimum efficiency and could possibly not work at all if a sufficient amount of the charge control agent does not remain on the particles. In order to resolve this problem, the present invention uses particles, and preferably pigments, having attached at least one type of organic group. The use of such modified particles have several advantages from previous electrophoretic displays. First of all, by using a modified particle which has attached at least one organic group, wherein the organic group contains at least one ionic and/or ionizable group, no surface charge control agents are needed and through the attachment of the organic group, the problem of the charge-control agent being removed from the particle due to use or the effects of the dielectric fluid are not a concern due to the chemical attachment of the organic group onto the particles.

In addition, in making the microscopic containers for the arrangement which is located between the two electrodes, typically, a suspension or coacervation type polymerization is used which causes the encapsulation of the dielectric liquid and the particles. In achieving the formation of such microscopic containers, it is preferred to have a uniform suspension of particles in the dielectric fluid in order to encapsulate an even distribution of dielectric fluid along with particles. The present invention makes this quite possible since the particles of the present invention which have attached organic groups having at least one ionic and/or ionizable group are substantially and uniformly suspended in a dielectric fluid which can be hydrophobic, for instance, without the need of suspension aids and the like. Accordingly, the present invention enables a uniform distribution of particles in dielectric fluids in the formation of the microscopic containers and further leads to maintaining this suspension throughout the use of the electrophoretic display. Thus, the problems of agglomeration can be significantly avoided.

The benefits of the present invention can be used in the electrophoretic displays, for instance, described in U.S. Patent Nos. 5,930,026; 5,961,804; and 6,017,584, all incorporated in their entirety by reference herein.

The arrangement can be any shape, such as flat or curved and typically is a two-dimensional arrangement which has various thicknesses. The arrangement can be accomplished by packing the microcontainers against one another in an array or dispersing the microscopic containers in a transparent matrix and the like. Various microencapsulation

techniques can be used to create the microscopic containers including those described for instance, in U.S. Patent Nos. 4,001,140; 4,273,672; and 3,585,381, all incorporated in their entirety by reference herein.

The display that is used in the present invention can be any conventional display used  
5 to display images such as those used in liquid-crystal displays. The microscopic containers, for instance, can be inserted into a cell housing the two electrodes. The microscopic containers can also be applied into a display by any various means known to those skilled in the art involving the insertion of microcapsules on a substrate. The display can be arranged in any number of designs including unitary displays, continuous displays, and the like.

10 The non-emissive display system essentially involves the same components described above wherein the non-emissive display system involves two electrodes wherein a display element is located between the electrodes. The display element contains the arrangement of microscopic containers as described above wherein the containers contain a dielectric fluid and the modified particles. The display element is visually responsive to a potential  
15 difference created between the electrodes. The non-emissive display system further involves a display piezoelectric element which is connected to the electrodes wherein deformation of this piezoelectric element produces the potential difference which causes the particles in the microscopic containers to migrate to one of the electrodes. The display piezoelectric element can be any conventional element known to those skilled in the art such as those described in  
20 the patents referred to above.

The pigment can be, but is not limited to, pigments traditionally used in ink compositions (including inkjet ink compositions), coating compositions (including paint formulations), liquid and solid toners, films, plastics, rubbers, and the like. Examples include, but are not limited to, black pigments (e.g., carbon products like carbon black) and  
25 other colored pigments (e.g., polymeric and organic pigments).

The desired colored pigment may be chosen from a wide range of conventional colored pigments.

For instance, the pigment product can be any carbon product capable of reacting with a diazonium salt to form the modified pigment product. The carbon may be of the crystalline  
30 or amorphous type. Examples include, but are not limited to, graphite, carbon black, vitreous carbon, activated charcoal, activated carbon, carbon fibers, and mixtures thereof. Finely

divided forms of the above are preferred. It is also possible to utilize mixtures of different pigment products.

The colored pigment can be blue, black, brown, cyan, green, white, violet, magenta, red, yellow, as well as mixtures thereof. Suitable classes of colored pigments include, for example, carbon black, carbon products, anthraquinones, phthalocyanine blues, phthalocyanine greens, diazos, monoazos, pyranthrones, perylenes, heterocyclic yellows, quinacridones, and (thio)indigoids. Representative examples of phthalocyanine blues include copper phthalocyanine blue and derivatives thereof (Pigment Blue 15). Representative examples of quinacridones include Pigment Orange 48, Pigment Orange 49, Pigment Red 122, Pigment Red 192, Pigment Red 202, Pigment Red 206, Pigment Red 207, Pigment Red 209, Pigment Violet 19 and Pigment Violet 42. Representative examples of anthraquinones include Pigment Red 43, Pigment Red 194 (Perinone Red), Pigment Red 216 (Brominated Pyanthrone Red) and Pigment Red 226 (Pyranthrone Red). Representative examples of perylenes include Pigment Red 123 (Vermillion), Pigment Red 149 (Scarlet), Pigment Red 179 (Maroon), Pigment Red 190 (Red), Pigment Violet 19, Pigment Red 189 (Yellow Shade Red) and Pigment Red 224. Representative examples of thioindigoids include Pigment Red 86, Pigment Red 87, Pigment Red 88, Pigment Red 181, Pigment Red 198, Pigment Violet 36, and Pigment Violet 38. Representative examples of heterocyclic yellows include Pigment Yellow 1, Pigment Yellow 3, Pigment Yellow 12, Pigment Yellow 13, Pigment Yellow 14, Pigment Yellow 17, Pigment Yellow 65, Pigment Yellow 73, Pigment Yellow 74, Pigment Yellow 151, Pigment Yellow 117, Pigment Yellow 128 and Pigment Yellow 138. Such pigments are commercially available in either powder or press cake form from a number of sources including, BASF Corporation, Engelhard Corporation and Sun Chemical Corporation. Examples of other suitable colored pigments are described in the Colour Index, 3rd edition (The Society of Dyers and Colourists, 1982). The color pigment will typically have a wide range of BET surface areas, as measured by nitrogen adsorption.

Also, for purposes of the present invention, the carbonaceous material can be an aggregate comprising a carbon phase and a silicon-containing species phase. A description of this aggregate as well as means of making this aggregate is described in PCT Publication No. WO 96/37547 and WO 98/47971 as well as U.S. Patent Nos. 5,830,930; 5,869,550; 5,877,238; 5,919,841; 5,948,835; and 5,977,213. All of these patents and publications are hereby incorporated in their entireties herein by reference.



The carbonaceous material for purposes of the present invention, can also be an aggregate comprising a carbon phase and metal-containing species phase where the metal-containing species phase can be a variety of different metals such as magnesium, calcium, titanium, vanadium, cobalt, nickel, zirconium, tin, antimony, chromium, neodymium, lead, tellurium, barium, cesium, iron, molybdenum, aluminum, and zinc, and mixtures thereof. The aggregate comprising the carbon phase and a metal-containing species phase is described in U.S. Patent No. 6,017,980, also hereby incorporated in its entirety herein by reference.

Also, for purposes of the present invention, the carbonaceous material includes a silica-coated carbon black, such as that described in U.S. Patent No. 5,916,934 and PCT Publication No. WO 96/37547, published November 28, 1996, also hereby incorporated in their entirety herein by reference.

With respect to the particle size of the colored pigments, the particle size distribution is based on the mean volume diameter of the pigment particles as measured by the dynamic light scattering method. The particle size distribution range of the colored pigments of the present invention is from about 10 nm to about 300 nm, and preferably is from about 10 nm to about 200 nm, more preferably is from about 20 nm to about 150 nm, and most preferably is from about 50 nm to about 100 nm.

As indicated above, the modified particle is preferably a colored pigment having attached at least one organic group. The organic group preferably contains a) at least one aromatic group, at least one C<sub>1</sub>-C<sub>100</sub> alkyl group, or mixtures thereof; and further contains b) at least one ionic group, ionizable group, or mixtures thereof.

At least one aromatic group includes, but is not limited to, unsaturated cyclic hydrocarbons containing one or more rings and may be substituted or unsubstituted, for example with alkyl groups. Aromatic groups include aryl groups (for example, phenyl, naphthyl, anthracenyl, and the like) and heteroaryl groups (for example, imidazolyl, pyrazolyl, pyridinyl, thienyl, thiazolyl, furyl, triazinyl, indolyl, and the like). At least one C<sub>1</sub>-C<sub>100</sub> alkyl group may be branched or unbranched, substituted or unsubstituted.

An ionizable group is one capable of forming an ionic group in the medium of use. The ionic group may be an anionic group or a cationic group and the ionizable group may form an anion or cation.

Ionizable functional groups forming anions or anionic groups include, for example, acidic groups or salts of acidic groups. The organic groups, therefore, include groups derived from organic acids. Preferably, when an organic group contains an ionizable group forming an anion, such an organic group has a) an aromatic group or a C<sub>1</sub>-C<sub>100</sub> alkyl group and b) at least one acidic group having a pK<sub>a</sub> of less than 11, or at least one salt of an acidic group having a pK<sub>a</sub> of less than 11, or a mixture of at least one acidic group having a pK<sub>a</sub> of less than 11 and at least one salt of an acidic group having a pK<sub>a</sub> of less than 11. The pK<sub>a</sub> of the acidic group refers to the pK<sub>a</sub> of the organic group as a whole, not just the acidic substituent.

More preferably, the pK<sub>a</sub> is less than 10 and most preferably less than 9. Preferably, the aromatic group or the alkyl group of the organic group is directly attached to the colored pigment. The aromatic group may be further substituted or unsubstituted, for example, with alkyl groups. More preferably, the organic group is a phenyl or a naphthyl group and the acidic group is a sulfonic acid group, a sulfinic acid group, a phosphonic acid group, or a carboxylic acid group. Most preferably, the organic group is a substituted or unsubstituted sulfophenyl group or a salt thereof; a substituted or unsubstituted carboxyphenyl; a substituted or unsubstituted (polysulfo)phenyl group or a salt thereof; a substituted or unsubstituted sulfonaphthyl group or a salt thereof; or a substituted or unsubstituted (polysulfo)naphthyl group or a salt thereof.

Specific organic groups having an ionizable functional group forming an anion (and their corresponding primary amines) are p-sulfophenyl (p-sulfanilic acid), 4-hydroxy-3-sulfophenyl (2-hydroxy-5-amino-benzenesulfonic acid), and 2-sulfoethyl (2-aminoethanesulfonic acid). Other organic groups having ionizable functional groups forming anions can also be used.

Examples of organic groups that are anionic in nature include, but are not limited to, -C<sub>6</sub>H<sub>4</sub>-COO<sup>-</sup>X<sup>+</sup>; -C<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub><sup>-</sup>X<sup>+</sup>; -C<sub>6</sub>H<sub>4</sub>-(PO<sub>3</sub>)<sup>-2</sup>2X<sup>+</sup>; -C<sub>6</sub>H<sub>2</sub>-(COO<sup>-</sup>X<sup>+</sup>)<sub>3</sub>; -C<sub>6</sub>H<sub>3</sub>-(COO<sup>-</sup>X<sup>+</sup>)<sub>2</sub>; -(CH<sub>2</sub>)<sub>z</sub>-(COO<sup>-</sup>X<sup>+</sup>); -C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>z</sub>-(COO<sup>-</sup>X<sup>+</sup>), wherein X<sup>+</sup> is any cation such as Na<sup>+</sup>, H<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and the like and z is an integer from 1 to 18. As recognized by those skilled in the art, X<sup>+</sup> may be formed *in-situ* as part of the manufacturing process or may be associated with the aromatic or alkyl group through a typical salt swap or ion-exchange process.

Amines represent examples of ionizable functional groups that form cations or cationic groups and may be attached to the same groups as discussed above for the ionizable

groups which form anions. For example, amines may be protonated to form ammonium groups in acidic media. Preferably, an organic group having an amine substituent has a  $pK_b$  of less than 5. Quaternary ammonium groups ( $-NR_3^+$ ), quaternary phosphonium groups ( $-PR_3^+$ ) and sulfonium groups ( $-SR_2^+$ ) also represent examples of cationic groups. Preferably, the organic group contains an aromatic group such as a phenyl or a naphthyl group and a quaternary ammonium or a quaternary phosphonium or sulfonium group. Quaternized cyclic amines, and even quaternized aromatic amines, can also be used as the organic group. Thus, N-substituted pyridinium compounds, such as N-methyl-pyridyl, can be used in this regard.

Examples of organic groups that are cationic in nature include, but are not limited to,  $-C_6H_4N(CH_3)_3^+Y^-$ ,  $-C_6H_4COCH_2N(CH_3)_3^+Y^-$ ,  $-C_6H_4(NC_5H_5)^+Y^-$ ,  $-(C_5H_4N)C_2H_5^+Y^-$ ,  $-(C_3H_5N_2)^+Y^-$  (imidizoles),  $-(C_7H_7N_2)^+Y^-$  (indizoles),  $-C_6H_4COCH_2(NC_5H_5)^+Y^-$ ,  $-(C_5H_4N)CH_3^+Y^-$ , and  $-C_6H_4CH_2N(CH_3)_3^+Y^-$ , wherein  $Y^-$  is any halide or an anion such as  $NO_3^-$ ,  $OH^-$ ,  $CH_3COO^-$  and the like; or combinations thereof. As recognized by those skilled in the art,  $Y^-$  may be formed *in-situ* as part of the manufacturing process or may be associated with the aromatic or alkyl group through a typical salt swap or ion-exchange process.

Further examples of representative organic groups and methods of attachment are also described in U.S. Patent Nos. 5,554,739; 5,559,169; 5,571,311; 5,575,845; 5,630,868; 5,672,198; 5,698,016; 5,837,045; 5,922,118; 5,968,243; 6,042,643; 5,900,029; 5,955,232; 5,895,522; 5,885,335; 5,851,280; 5,803,959; 5,713,988; 5,707,432; and 6,110,994; and International Patent Publication Nos. WO 97/47691; WO 99/23174; WO 99/31175; WO 99/51690; WO 99/63007; and WO 00/22051; all hereby incorporated in their entirety by reference herein. The groups and methods of attachments described in International Published Application Nos. WO 99/23174 and WO 99/63007, can also be used and are incorporated in their entirety by reference herein.

Further examples of the ionic or ionizable functional groups include amphiphilic counterions which may be cationic or anionic in nature. An amphiphilic counterion is a molecule or compound typically described as have a hydrophilic polar "head" and a hydrophobic "tail." Representative examples of cationic and anionic amphiphilic counterions include those set forth and described in U.S. Patent No. 5,698,016 to Adams et al., the entire description of which is incorporated herein by reference.

For purposes of further illustrating the present invention, an amphiphilic counterion can be used. The surface-modified colored pigment, as described herein, preferably has a

cationic functionality (i.e. positive charge) or anionic functionality (negative charge). The charge preferably is created by the ionic or ionizable group of the aromatic group or C<sub>1</sub>-C<sub>100</sub> alkyl group attached to the pigment. If the desired surface-modified colored pigment is anionic in nature, then the amphiphilic counterion will be cationic or positive charging.

5 Similarly, if the surface-modified colored pigment is cationic in nature, then the amphiphilic counterion will be anionic or negative charging. Examples of cationic amphiphilic counterions include, but are not limited to, those described ammonium ions that may be formed from adding acids to the following: a fatty amine, an ester of an aminoalcohol, an alkylamine, a polymer containing an amine functionality, a polyethoxylated amine, a

10 polypropoxylated amine, a polyethoxylated polypropoxylated amine, an aniline and derivatives thereof, a fatty alcohol ester of amino acid, a polyamine N-alkylated with a dialkyl succinate ester, a heterocyclic amine, a guanidine derived from a fatty amine, a guanidine derived from an alkylamine, a guanidine derived from an arylamine, an amidine derived from a fatty amine, an amidine derived from a fatty acid, an amidine derived from an

15 alkylamine, or an amidine derived from an arylamine. The pK<sub>a</sub> of the ammonium ion is preferably greater than the pK<sub>a</sub> of the protonated form of the aromatic or alkyl group on the pigment.

Specific examples of cationic amphiphilic ions include dioctylammonium, oleylammonium, stearylammmonium, dodecylammonium, dimethyldodecylammonium,

20 stearylguanidinium, oleylguanidinium, soyalkylammonium, cocoalkylammonium, oleylammoniummethoxylate, protonated diethanolaminedimyristate, and N-oleyldimethylammonium. Generally, to form the ammonium ions described above, the various compounds described above such as fatty amines, esters of amino alcohols, etc., are reacted with an acid such as carboxylic acid, a mineral acid, an alkyl sulfonic acid, or an aryl

25 sulfonic acid.

Quaternary ammonium salts can also be used as the sources of the cationic amphiphilic ion. Examples include, but are not limited to, a fatty alkyl trimethyl ammonium, a di(fatty alkyl)dimethylammonium, an alkyl trimethyl ammonium, or 1-alkyl pyridinium salt, where the counterion is a halide, methosulfate, sulfonate, a sulfate or the like. Also,

30 phosphonium salts, such as tetraphenylphosphonium chloride can be used as the sources of the amphiphilic ion.

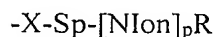
Cationic amphiphilic ions for use in the present invention include those represented by the formula  $R_4N^+$ , wherein R is independently hydrogen, C<sub>1</sub>-C<sub>30</sub> alkyl, C<sub>1</sub>-C<sub>30</sub> alkenyl, C<sub>7</sub>-C<sub>30</sub> aralkyl, and C<sub>7</sub>-C<sub>30</sub> alkaryl. Another example of a suitable amphiphilic ion is a polymer containing an ammonium ion derived from an amine containing polymer. The amine containing polymer can be a copolymer of an amine containing monomer, such as dimethylaminoethyl methacrylate or -acrylate, or vinylpyridine or vinylimidazole, and another monomer such as methyl acrylate, methyl methacrylate, butyl acrylate, styrene, and the like. The polymer may also be a polyethyleneimine (PEI) derivitized or acylated PEI, polyallylamine, or polydiallylamine. The polymer may also be a ter- or tetra-polymer containing a mixture of an amine containing monomer and two or three other amine containing monomers, respectively. Such a polymer may be prepared by any means, such as radical (emulsion, suspension, or solution) or anionic polymerization, stable free radical polymerization or atom transfer polymerization.

As stated earlier, the amphiphilic counterion can alternatively be an anionic amphiphilic counterion. Examples of such anionic amphiphilic ions include, but are not limited to, an alkylbenzene sulfonate, an alkyl sulfonate, an alkylsulfate, a sulfosuccinate, a sarcosine, an alcohol ethoxylate sulfate, an alcohol ethoxylate sulfonate, an alkyl phosphate, an alkylethoxylated phosphate, an ethoxylated alkylphenol sulfate, a fatty carboxylate, a taurate, an isethionate, an aliphatic carboxylate, or an ion derived from a polymer containing an acid group. Sources of specific and preferred examples of anionic amphiphilic ions include, but are not limited to, sodium dodecylbenzene sulfonate, a sodium dodecylsulfate, Aerosol OT, an oleic acid salt, a ricinoleic acid salt, a myristic acid salt, a caproic acid salt, sodium 2-octyldodecanoate, sodium bis(2-ethylhexyl)sulfosuccinate, a sulfonated polystyrene, or homo- or copolymers of acrylic acid or methacrylic acid or salts thereof.

Generally, the above-identified amphiphilic counterions and related compounds are commercially available in salt form or can be routinely made by one of ordinary skill in the art.

Other examples of organic groups that can be attached onto the colored pigment include the following formulas. In each of the following formulas, -X is attached directly to the pigment and -X' can be directly attached to the pigment. Each of the following organic groups, for purposes of the present invention, further contain an ionic group, an ionizable group, or both.

A further example of modified pigment product is a colored pigment having attached at least one group comprising the formula:



wherein X represents an aromatic group or an alkyl group, Nlon represents at least one  
5 non-ionic group, Sp represents a spacer group, R represents hydrogen, an aromatic group, or an alkyl group, and p is an integer of from 1 to 500.

The aromatic group with respect to the X substituent and/or the R substituent can be substituted or unsubstituted and can be, for instance, an aryl or heteroaryl group. The aromatic group can be substituted with any group, such as one or more alkyl groups or aryl  
10 groups. Preferably, the aromatic group is a phenyl, naphthyl, anthracenyl, phenanthrenyl, biphenyl, pyridinyl, benzothiadiazolyl, or benzothiazolyl. Examples of the alkyl group with respect to the X substituent and/or the R substituent include, but are not limited to, substituted or unsubstituted alkyl groups which may be branched or unbranched. The alkyl group can be substituted with one or more groups, such as aromatic groups. Preferred  
15 examples of the alkyl group for purposes of the X substituent include, but are not limited to, C<sub>1</sub>-C<sub>12</sub>, like methyl, ethyl, propyl, butyl, pentyl, or hexyl groups. In other words, X and/or R can represent a branched or unbranched, substituted or unsubstituted, saturated or unsaturated hydrocarbon. Examples of substituted groups include, but are not limited to, an ester group, an amide group, an ether group, a carboxyl group, an aryl group, an alkyl  
20 group, and the like.

Sp or the spacer group as used herein is a link between two groups and can be a bond, or a chemical group such as, but not limited to, CO<sub>2</sub>, SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>, CHR"CH<sub>2</sub>, CH<sub>2</sub>CHR", CHR", O<sub>2</sub>C, SO<sub>2</sub>, CO, SO<sub>3</sub>, OSO<sub>2</sub>, SO<sub>3</sub>NR", R"NSO<sub>2</sub>, NHCO, CONR", NR"CO<sub>2</sub>, O<sub>2</sub>CNR", NR"CONR", O,S, NR", SO<sub>2</sub>C<sub>2</sub>H<sub>4</sub>, arylene, alkylene, NR"CO,  
25 NHCO<sub>2</sub>, O<sub>2</sub>CNH, NCHONH, and the like, wherein R", which can be the same or different, represents an organic group such as a substituted or unsubstituted aryl and/or alkyl group.

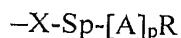
Examples of the non-ionic group include, but are not limited to, groups having no apparent ionic charge, such as polymers of ethylene oxide, propylene oxide, other alkylene oxides, carboxylic acid esters, glycols, alcohols, esters, alkanolamine-fatty acid  
30 condensates, silicones, isocyanates, alkylpyrrolidenes, and alkylpolyglycosides. In non-aqueous media, the non-ionic group, in addition to the aforementioned groups, may have carboxylates, sulfonates, phosphates, amines, and other groups that typically demonstrate

an ionic nature in water. The non-ionic group is preferably a C<sub>1</sub>-C<sub>12</sub> alkyl group, or a C<sub>1</sub>-C<sub>12</sub> alkylene oxide group. p can be 1-25, 26-50, 51-75, 75-100, and/or 101-500, and p preferably is 5 to 50.

The X substituent and/or non-ionic group may be substituted with one or more functional groups. The functional group preferably contains a lypophilic group. Examples of functional groups include, but are not limited to, R', OR', COR', COOR', OCOR', carboxylates, halogens, CN, NR'<sub>2</sub>, SO<sub>3</sub>H, sulfonates, -OSO<sub>3</sub><sup>-</sup>, NR'(COR'), CONR'<sub>2</sub>, NO<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, phosphonates, phosphates, N=NR', SOR', NSO<sub>2</sub>R', wherein R' which can be the same or different, is independently hydrogen, branched or unbranched C<sub>1</sub>-C<sub>20</sub> substituted or unsubstituted, saturated or unsaturated hydrocarbons, e.g., alkyl, alkenyl, alkynyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted or unsubstituted alkylaryl, or substituted or unsubstituted arylalkyl.

Amines also represent examples of functional groups as well as quaternary ammonium groups (-NR<sub>3</sub><sup>+</sup>) and quaternary phosphonium groups (-PR<sub>3</sub><sup>+</sup>), as well as quaternary sulfonium groups (-SR<sub>2</sub><sup>+</sup>).

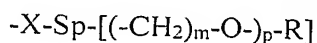
In an additional embodiment of the present invention, the colored pigment product can be a pigment having attached at least one group comprising the formula:



wherein X represents an aromatic group or an alkyl group; Sp represents a spacer group; A represents an alkylene oxide group of from about 1 to about 12 carbons; p represents an integer of from 1 to 500, and R represents hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aromatic group. A can be the same or different when p is greater than 1. X can be substituted or unsubstituted and can include substituted groups such as an ester group, an amide group, an ether group, a carbonyl group, an aryl group, an alkyl group and the like. The substituted groups can be attached or linked to A.

Examples of preferred alkylene groups include, but are not limited to, -CH<sub>2</sub>-CH<sub>2</sub>-O-; -CH(CH<sub>3</sub>)-CH<sub>2</sub>-O-; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O-; -CH<sub>2</sub>CHCH<sub>3</sub>-O-; or combinations thereof.

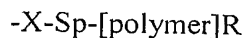
In another embodiment of the present invention, the colored pigment can be a pigment having attached at least one group comprising the formula:



wherein X is described above, and for instance can represent an aromatic group or an alkyl group as described earlier, m is an integer of from 1 to 12, preferably 2 or 3, p is an integer

of from 1 to 500, Sp represents a spacer group, and R is described above, and for instance can be hydrogen, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aromatic group. Examples of R substituents include, but are not limited to, hydrogen, methyl, ethyl, butyl, or propyl groups. p can be 1-25, 26-50, 51-75, 76-100, and 101-500, and is preferably 5 to 50. Particularly preferred groups of this formula are where X is a phenylene group, m is 1 to 5, and more preferably 2 or 3, p is 5 to 50, more preferably 44-45, and R is hydrogen or a methyl group. Another preferred group is where m is 2, p is 7, R is a methyl group, and X is a phenylene group.

In yet another embodiment of the present invention, the colored pigment can be a pigment having attached at least one polymeric group, wherein the polymeric group comprises the formula:



wherein X and Sp are described above, and for instance can represent at least an aromatic group or at least an alkyl group as described earlier, "polymer" comprises repeating monomer groups or multiple monomer groups or both, optionally having at least one -X' group. The 'polymer' can be substituted or unsubstituted with additional groups, and R is described above, and for instance can represent hydrogen, a bond, a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aromatic group. When X represents an alkyl group, the "polymer" preferably has no ionic or ionizable group. X' represents an aromatic group or alkyl group, and each X' and X can be the same or different. The total monomer repeating units that comprise the "polymer" is not greater than about 5,000 monomer repeating units. X and/or X' can be substituted or unsubstituted and can include substituted groups such as an ester group, an amide group, an ether group, and the like. The substituted groups can be linked to the "polymer." Also, when R represents a bond, the available bond can be attached to the pigment. When X represents an alkyl group in this formula, the polymeric group preferably has no ionic or ionizable group. The polymeric group can be any polymeric group capable of being attached to a pigment.

For purposes of the present invention and this formula immediately above, one or more polymeric groups that comprise the "polymer" can be present. The polymeric group can be a thermoplastic polymeric group or a thermosetting polymeric group. Further, the polymeric group can be a homopolymer, copolymer, terpolymer, and/or a polymer



containing any number of different repeating units. Further, the polymeric group present in the present invention can be any type of polymeric group, such as a random polymer, alternating polymer, graft polymer, block polymer, star-like polymer, and/or comb-like polymer. The polymeric group used in the present invention can also be one or more  
5 polyblends. The polymeric group can be an interpenetrating polymer network (IPN); simultaneous interpenetrating polymer network (SIN); or interpenetrating elastomeric network (IEN).

Specific examples of polymeric groups include, but are not limited to, linear-high polymers such as polyethylene, poly(vinylchloride), polyisobutylene, polystyrene,  
10 polycaprolactam (nylon), polyisoprene, and the like. Other general classes of polymeric groups of the present invention are polyamides, polycarbonates, polyelectrolytes, polyesters, polyethers, (polyhydroxy)benzenes, polyimides, polymers containing sulfur (such as polysulfides, (polyphenylene) sulfide, and polysulfones), polyolefins, polymethylbenzenes, polystyrene and styrene copolymers (ABS included), acetal  
15 polymers, acrylic polymers, acrylonitrile polymers and copolymers, polyolefins containing halogen (such as polyvinyl chloride and polyvinylidene chloride), fluoropolymers, ionomeric polymers, polymers containing ketone group(s), liquid crystal polymers, polyamide-imides, polymers containing olefinic double bond(s) (such as polybutadiene, polydicyclopentadiene), polyolefin copolymers, polyphenylene oxides, polysiloxanes,  
20 poly(vinyl alcohols), polyurethanes, thermoplastic elastomers, and the like.

Generally, the polymeric groups described in Volume 18 of the Encyclopedia of Chemical Technology, KIRK-OTHMER, (1982), page 328 to page 887, and Modern  
Plastics Encyclopedia '98, pages B-3 to B-210, and "Polymers: Structure and Properties,"  
by C.A. Daniels, Technomic Publishing Co., Lancaster, PA (1989), all incorporated in  
25 their entirety herein by reference, can be used as the polymeric groups of the present invention.

The polymeric groups of the present invention can be prepared in a number of ways and such ways are known to those skilled in the art. The above referenced KIRK-OTHMER section, Modern Plastics Encyclopedia, and C.A. Daniels' reference provide  
30 methods in which these polymeric groups can be prepared.

The polymeric group is preferably a polyolefin group, a polyurethane group, a polystyrenic group, a polyacrylate group, a polyamide group, a polyester group, or

mixtures thereof. Examples of R groups can be the same as previously described above. p can be 1-25, 26-50, 51-75, 76-100, 101-500, and is preferably 1 to 100, and more preferably 5 to 50.

Also, the organic group(s) attached to the colored pigment can be one or more types of dyes, such as, but not limited to, Nile Blue A, Toluidine Blue, Trypan Blue, C.I. Acid Blue 40, C.I. Acid Blue 129, C.I. Acid Blue 9, C.I. Acid Blue 185, C.I. Direct Blue 71, C.I. Direct Blue 199, C.I. Direct Red 9, C.I. Acid Red 18, C.I. Acid Red 27, C.I. Direct Yellow 86, C.I. Direct Yellow 4, C.I. Acid Yellow 23, and C.I. Food Black 2. Besides the organic group comprising the dye, an organic group having an ionic group and a counterionic group can have a dye serving as the counterionic group. Attaching a dye to the colored pigment can provide the advantage of modifying the color properties of pigments. Also, the organic group(s) attached to the colored pigment can be one or more types of light stabilizers, e.g., hindered amine light stabilizer (HALS) or antioxidant.

In an embodiment of the present invention, the modified particle can be a polymer coated modified pigment product. The modified pigment product is at least partially coated with one or more polymers and can be substantially or fully coated by one or more polymers. The use of the term "coated" includes partially and fully coated carbon products and modified pigment products. The polymer in this invention, partially or fully encapsulates the modified pigment product, wherein the modified pigment product is the core and the polymer is the shell. The polymer(s) coated onto or used to encapsulate the modified pigment product is preferably present on the modified pigment product such that the polymer(s) is not substantially extractable by a solvent. More preferably, the polymer(s) on the modified pigment product is attached by physical (e.g., adsorption) and/or chemical means (e.g. chemical bonding, grafting).

The pigment product coated with a polymer can be a modified pigment product having at least one organic group attached to the pigment product. Preferably, the organic group is substituted with an ionic, ionizable, or polar group. The pigment product which has the organic group attached thereto can be any pigment product capable of having at least one organic group attached to the pigment product.

Another set of organic groups which may be attached to the pigment are organic groups having an aminophenyl, such as  $(C_6H_4)-NH_2$ ,  $(C_6H_4)-CH_2-(C_6H_4)-NH_2$ ,  $(C_6H_4)-SO_2-(C_6H_4)-NH_2$ . Organic groups also include aromatic sulfides, represented, for instance, by the

formulas  $\text{Ar-S}_n\text{-Ar'}$  or  $\text{Ar-S}_n\text{-Ar''}$ , wherein Ar and Ar' are independently arylene groups, Ar'' is an aryl and n is 1 to 8.

Preferably, the organic group comprises an aromatic group and/or a  $\text{C}_1\text{-C}_{100}$  alkyl group (and more preferably a  $\text{C}_1\text{-C}_{12}$  alkyl group) directly attached to the pigment, preferably  
5 with an ionic, ionizable, or polar group.

More than one type of organic group can be attached to the pigment, or two or more modified pigments with different attached organic groups can be used. Using two or more different types of organic groups permits a combination of properties. If two different types of organic groups are attached, for example, a sulfanilic group and a styrenic group, the  
10 sulfanilic group promotes dispersibility and the styrenic group serves as a radical grafting site. The ratio of the different organic groups can be the same or different. Preferably, only the minimum treatment level of the ionic, ionizable, or polar group is used to impart stability to the dispersion. For example, groups such as ionic species (*e.g.*, sulphates, phosphates, alkali salts of organic acids or quaternary ammonium salts), non-ionic species (*e.g.*,  
15 hydroxyl, organic acids) or surfactant stabilizers (*e.g.*, SDMS, SDS, Antarox) can be used to provide stable pigment dispersions in aqueous media. Dispersion of the modified pigment in organic liquids can be facilitated in a similar manner but employing treatments which are more compatible with these less polar environments. Treatment levels of the organic group for purposes of radical grafting sites would depend on material uses. For instance, attachment  
20 of epoxy groups would facilitate grafting to hydroxyl bearing polymer matrices such as polyurethanes or polycarbonates or amine matrices such as nylon. Other examples include the attachment of radical sensitive vinyl groups such as styrenics or acrylates, or methacrylates, to facilitate crosslinking type reactions in radical polymerizations.

Also, a combination of different modified pigment can be used. For instance, a  
25 modified pigment having one type of organic group attached thereto can be used in combination with another modified pigment having a different organic group attached thereto. Also, a modified pigment such as an aggregate comprising a carbon phase and a silicon-containing species phase can be used in combination with a modified carbon product having an attached organic group, and so on.

30 The modified pigment which is coated with one or more polymers can have any particle size and/or surface area so long as the particle is capable of being at least partially coated with one or more polymers. Preferably, the primary particle size of the modified

pigment is from about 5 nm to about 100 nm and more preferably from about 8 nm to about 75 nm. The nitrogen surface area as measured by the BET method, of the modified carbon product is preferably from about 20 m<sup>2</sup>/g to about 1500 m<sup>2</sup>/g and more preferably from about 25 m<sup>2</sup>/g to about 700 m<sup>2</sup>/g and most preferably from about 30 m<sup>2</sup>/g to about 250 m<sup>2</sup>/g.

5       The thickness of the coating on the modified pigment can be uniformed or can vary in thickness. The thickness of the coating can be about 1 nm or more. Preferably, the polymer coated onto the modified carbon product is substantially uniform in thickness. Preferably, the thickness of the polymer coating on the modified pigment is from about 10 nm to about 100 nm, more preferably from about 20 nm to about 75 nm, and most preferably  
10       from about 30 nm to about 50 nm.

      The modified carbon product can have more than one coating or shell. In other words, the modified pigment can have multiple layers of shells or coatings which partially or fully encapsulate the modified carbon product or a previous coating or shell. The polymers comprising the various layers can be the same or different. For instance, one layer can be  
15       cross-linked while the next layer can be not cross-linked. Each of the various coatings, if more than one is present on the modified carbon product, can be substantially the same or vary in thickness if desired.

      The polymer which is coated onto the modified carbon product can be a homopolymer, copolymer, terpolymer, and/or a polymer containing any number of different  
20       repeating units.

      The polymer can be any type of polymer, such as a random polymer, alternating polymer, graft polymer, block polymer, star-like polymer, and/or comb-like polymer. The polymer can also be one or more polyblends. The polymer can be an interpenetrating polymer network (IPN); simultaneous interpenetrating polymer network (SIN); or  
25       interpenetrating elastomeric network (IEN). The polymer can be thermoplastic or thermosettable.

      Specific examples of polymers include, but are not limited to, linear and non-linear polymers such as polyethylene, poly(vinylchloride), polyisobutylene, polystyrene, polycaprolactam (nylon), polyisoprene, and the like. Other general classes of polymers  
30       include polyamides, polycarbonates, polyelectrolytes, polyesters, polyethers, (polyhydroxy)benzenes, polyimides, polymers containing sulfur (such as polysulfides, (polyphenylene) sulfide, and polysulfones, polyolefins, polymethylbenzenes, polystyrene and

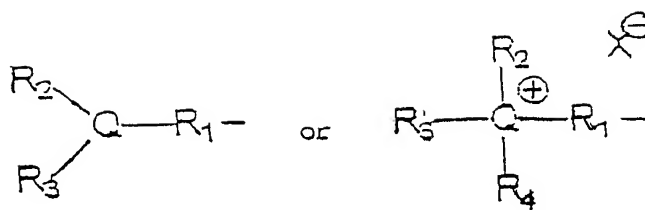
styrene copolymers (ABS included), acetal polymers, acrylic polymers, acrylonitrile polymers and copolymers, polyolefins containing halogen (such as polyvinyl chloride and polyvinylidene chloride), fluoropolymers, ionomeric polymers, polymers containing ketone group(s), liquid crystal polymers, polyamide-imides, polymers containing olefinic double bond(s) (such as polybutadiene, polydicyclopentadiene), polyolefin copolymers, polyphenylene oxides, polyurethanes, thermoplastic elastomers, silicone polymers, alkyd, epoxy, unsaturated polyester, vinyl ester, urea-, melamine-, or phenol-formaldehyde resins, and the like. Preferably, the polymer is an acrylic polymer, a methacrylic polymer, or a styrenic polymer, but would largely depend upon the intended application. For instance, reinforcement applications would generally involve the formation of a rubber product that could be attached to the modified carbon product in a manner such that the rubber product is preferably not extractable, *e.g.*, not extractable in solvents. This can be accomplished by using a modified carbon product that has styrenic groups attached to the surface. During an aqueous media radical polymerization, the propagating chains could graft to these sites on the surface of the modified carbon product and generate a rubbery coated particle.

The polymer coated modified pigments can be made by a number of ways. Preferably, the modified pigments are made by, but are not limited to, aqueous mediated polymerization environments such as emulsion polymerization or suspension polymerization processes as well as solvent based polymerizations. The polymerizations involved are generally chain growth polymerizations and/or step growth polymerizations.

In another embodiment, the modified pigment has at least one organic group attached to the pigment particles and the organic group is positively chargeable. The organic group can be attached to the pigment in various amounts, *i.e.*, low to high amounts, thus allowing fine control over charge modification. The organic group that is attached to the pigment particles can be any group which permits the modified pigment to be positively chargeable once incorporated into the dielectric fluid. Preferably, the organic group comprises an aromatic group or a C<sub>1</sub>-C<sub>20</sub> alkyl group, wherein either group can be substituted or unsubstituted. It is also preferred that the aromatic group or C<sub>1</sub>-C<sub>20</sub> alkyl group is directly attached to the pigment particles. Preferred groups of positively chargeable organic groups are nitrogen containing or phosphorus containing organic groups.

Preferred positive chargeable organic groups have the general structures:

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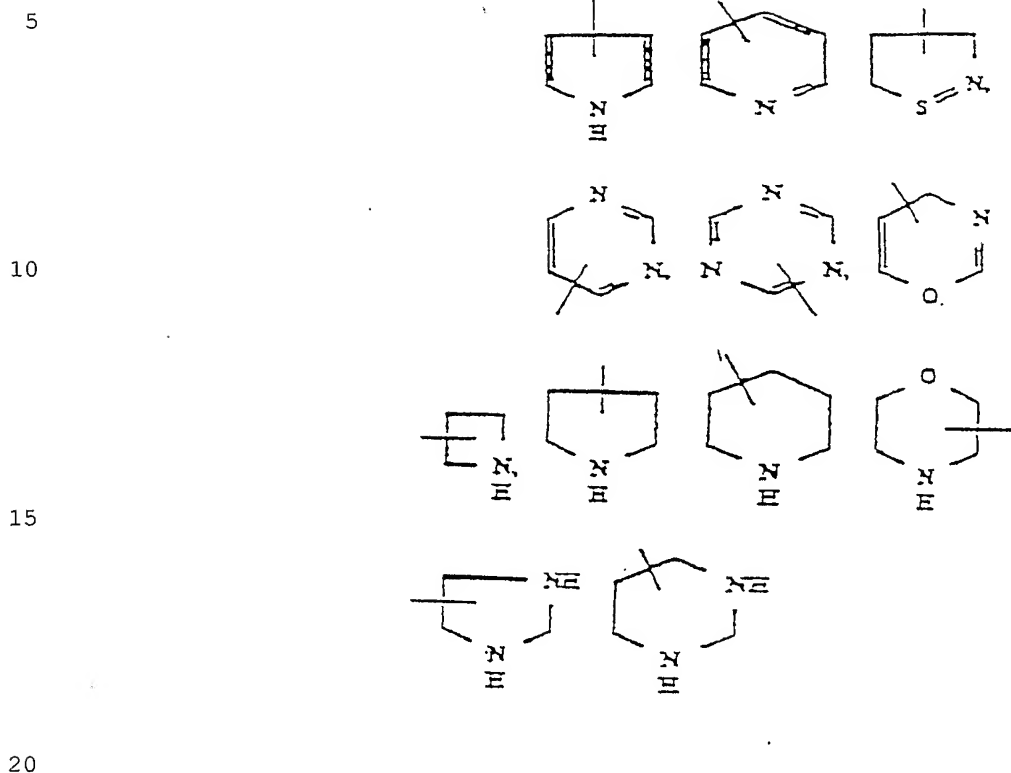


wherein Q represents the elements nitrogen or phosphorus; X represents a counterion such as  $Cl^-$ ,  $Br^-$ ,  $ArSO_3^-$ , and the like;  $R_1$  represents an alkylene group or an arylene group attached to the pigment; and  $R_2$ ,  $R_3$ , and  $R_4$ , which may be the same or different, each represent an alkyl group or an aryl group. Preferably, the alkylene or alkyl group is a  $C_1$ - $C_{10}$  alkylene or alkyl group and the arylene or aryl group is a  $C_6$ - $C_{20}$  arylene or aryl group. For the purposes of this invention, aryl and arylene groups include heteroaryl and heteroarylene groups, respectively.

Other preferred organic groups that can be attached to the pigment particles include, but are not limited to the following:

- |    |                                |                                             |
|----|--------------------------------|---------------------------------------------|
| 15 | $(C_4H_9)NHCH_2CH_2CH_2-$      | $NH_2CH_2CH_2-$                             |
|    | $(C_4H_9)_2NCH_2CH_2CH_2-$     | $NH_2CH_2CH_2CH_2-$                         |
|    | $(C_8H_{17})NHCH_2CH_2CH_2-$   | $NH_2CH_2CH_2CH_2CH_2-$                     |
|    | $(CH_8H_{17})_2NCH_2CH_2CH_2-$ | $NH_2CH_2CH_2CH_2CH_2CH_2-$                 |
| 20 | $ArNHCH_2CH_2-$                | $NH_2CH_2CH_2NHCH_2CH_2CH_2-$               |
|    | $ArNHCH_2CH_2CH_2-$            | $NH_2CH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2CH_2-$ |
|    | $ArNHCH_2CH_2CH_2CH_2-$        | $(CH_3)NHCH_2CH_2CH_2-$                     |
|    | $ArNHCH_2CH_2CH_2CH_2CH_2-$    | $(CH_3)_2NHCH_2CH_2CH_2-$                   |
| 25 | $ArAr'NCH_2CH_2-$              | $(C_2H_5)NHCH_2CH_2CH_2-$                   |
|    | $ArAr'NCH_2CH_2CH_2-$          | $(C_2H_5)_2NCH_2CH_2CH_2-$                  |
|    | $ArAr'NCH_2CH_2CH_2CH_2-$      | $-C_6H_4(NC_5H_5)^+X^-$ (as defined above)  |
|    | $ArAr'NCH_2CH_2CH_2CH_2CH_2-$  | $-C_5H_4N(CH_3)^+X^-$ (as defined above)    |

- $\text{NH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $(\text{CH}_3)\text{HCONHCH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $(\text{CH}_3)_2\text{NCONHCH}_2\text{CH}_2\text{CH}_2\text{-}$   
5  $(\text{C}_2\text{H}_5)\text{NHCONHCH}_2\text{CH}_2\text{CH}_2\text{-}$   $-\text{Ar-SO}_2\text{NH}(\text{C}_4\text{H}_3\text{N}_2)$   
 $(\text{C}_2\text{H}_5)_2\text{NCONHCH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $(\text{C}_4\text{H}_9)\text{NHCONHCH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $(\text{C}_4\text{H}_9)_2\text{NCONHCH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $\text{CH}_3\text{OCOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{-}$   
10  $(\text{C}_2\text{H}_5)\text{OCOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $(\text{C}_4\text{H}_9)\text{OCOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{-}$
- $\text{NH}_2\text{Ar-}$   
15  $(\text{CH}_3)\text{NHAr-}$   
 $(\text{CH}_3)_2\text{NAr-}$
- $\text{NH}_2\text{CH}_2\text{Ar-}$   
 $(\text{CH}_3)_2\text{NCH}_2\text{Ar-}$   
20  $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{Ar-}$   
 $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ar-}$   
 $(\text{CH}_3)\text{NHCH}_2\text{CH}_2\text{Ar-}$   
 $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{Ar-}$
- 25  $\text{Cl}^-(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $\text{Cl}^-(\text{C}_2\text{H}_5)_3\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $\text{Cl}^-(\text{C}_4\text{H}_9)_3\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $\text{Cl}^-(\text{C}_2\text{H}_5)(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $\text{Cl}^-(\text{C}_4\text{H}_9)(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$   
30  $\text{Cl}^-(\text{C}_8\text{H}_{17})(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{-}$   
 $(\text{HOCH}_2\text{CH}_2)_2\text{NAr-}$



in which Ar represents an aromatic group and Ar' represents an aromatic group. The aromatic group includes, but is not limited to, unsaturated cyclic hydrocarbons containing one or more rings. The aromatic group may be substituted or unsubstituted. Aromatic groups include aryl groups (*for example*, phenyl, naphthyl, anthracenyl, and the like), and heteroaryl groups (imidazolyl, pyrazolyl, pyridinyl, thienyl, thiazolyl, furyl, triazinyl, indolyl, and the like). In a similar manner, negatively chargeable particles can be produced using the appropriate functional groups, such as sulfamides.

A combination of organic groups such as an organic group comprising a pyridyl group and an organic group comprising a quaternary ammonium group can be used.

As stated, the organic group is a C<sub>1</sub>-C<sub>100</sub> alkyl group (more preferably a C<sub>1</sub>-C<sub>12</sub> alkyl group), an aromatic group, or other organic group, monomeric group, or polymeric group,



each optionally having a functional group or ionic or ionizable group. More preferably, these groups are directly attached to the particles.

The polymeric group can be any polymeric group capable of being attached to a particle. The polymeric group can be a polyolefin group, a polystyrenic group, a  
 5 polyacrylate group, a polyamide group, a polyester group, or mixtures thereof. Monomeric groups are monomeric versions of the polymeric groups.

The organic group can also be an olefin group, a styrenic group, an acrylate group, an amide group, an ester, or mixtures thereof. The organic group can also be an aromatic group or an alkyl group, either group with an olefin group, a styrenic group, an acrylate  
 10 group, an amide group, an ester group, or mixtures thereof, wherein preferably the aromatic group, or the alkyl group, like a C<sub>1</sub>-C<sub>12</sub> group, is directly attached to the particle.

The polymeric group can include an aromatic group or an alkyl group, like a C<sub>1</sub>-C<sub>12</sub> group, either group with a polyolefin group, a polystyrenic group, a polyacrylate group, a polyamide group, an polyester group, or mixtures thereof.

15 The organic group can also comprise an aralkyl group or alkylaryl group, which is preferably directly attached to the carbon product. Other examples of organic groups include a C<sub>1</sub>-C<sub>100</sub> alkyl group, and more preferably a C<sub>20</sub>-C<sub>60</sub> alkyl group.

Examples of other organic groups are organic groups having the following formulas (hyphens on one or more ends represents an attachment to a particle or to another  
 20 group):

- Ar-CO<sub>2</sub>(C<sub>m</sub>H<sub>2m+1</sub>), where m = 0 to about 20;
- Ar-(C<sub>n</sub>H<sub>2n+1</sub>), where n = 1 to about 50;
- Ar-C<sub>p</sub>H<sub>2p</sub> Ar-, where p = 1 to about 10;
- Ar-CX<sub>3</sub>, where X is a halogen atom;
- 25 -Ar-O-CX<sub>3</sub>, where X is a halogen atom;
- Ar-SO<sub>3</sub><sup>-</sup>;
- Ar-SO<sub>2</sub>(C<sub>q</sub>H<sub>2q-1</sub>), where q = about 2 to about 10;
- Ar-S<sub>2</sub>-Ar-NH<sub>2</sub>;
- Ar-S<sub>2</sub>-Ar-;
- 30 -ArSO<sub>2</sub>H;
- Ar-((C<sub>n</sub>H<sub>2n</sub>)COOX)<sub>m</sub>, where n=0 to 20, m=1 to 3, and X=H, cations, or organic group; These groups can be further activated and/or reacted with such groups as

carbodiimides and further reacted with  $\text{NH}_2$ -terminated functionalization groups;  $\text{SOCl}_2$ , or  $\text{PCl}_3$ , or  $\text{PCl}_5$  to be converted to  $-\text{Ar}-(\text{C}_n\text{H}_{2n})\text{COCl})_m$  groups and further reacted with OH-terminated functionalization groups.

5  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{OH})_m$ , where  $n=0$  to 20,  $m=1$  to 3; These groups can be further activated and/or reacted with such groups as tosyl chloride and subsequently reacted with amino-terminated ligands; carbonyldiimidazole and subsequently reacted with amino-terminated ligands; carbonylchloride terminated ligands; and epoxy terminated ligands.

10  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{NH}_2)_m$ , where  $n=0$  to 20,  $m=1$  to 3, and its protonated form:  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{NH}_3\text{X})_m$ , where X is an ion; These groups can be further activated and/or reacted with such groups as carbodiimide activated carboxyl-terminated ligands; carbonyldiimidazole activated hydroxy-terminated ligands; tosyl activated hydroxy-terminated ligands; vinyl terminated ligands; alkylhalide terminated ligands; or epoxy terminated ligands.

15  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{CHNH}_3^+\text{COO}^-)_m$  where  $n=0$  to 20 and  $m=1$  to 3; These groups can be derivatized further by reaction through the carboxylic group by reaction with  $\text{NH}_2$  or OH terminated groups or through the amino group by reaction with activated carboxy-terminated ligands, activated hydroxy-terminated ligands, vinyl ligands, alkylhalide terminated ligands, or epoxy terminated ligands.

20  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{CH}=\text{CH}_2)_m$ , where  $n=0$  to 20,  $m=1$  to 3 or  $-\text{Ar}-((\text{C}_n\text{H}_{2n})\text{SO}_2\text{CH}=\text{CH}_2)_m$ , where  $n=0$  to 20,  $m=1$  to 3. These groups can be further activated and/or reacted with such groups as amino-terminated ligands; peroxy-acids to form epoxides and subsequently reacted with hydroxy- or amino-terminated ligands; hydrogen halides to form  $-\text{Ar}((\text{C}_n\text{H}_{2n})\text{CH}_2\text{CH}_2\text{X})_m$  groups and subsequently reacted with amino-terminated ligands.

25 or mixtures thereof. Other reaction schemes can be used to form various groups onto the particles.

Other mixtures of organic groups include the following:

30  $-\text{Ar}-\text{SO}_3^-$  and  $-\text{Ar}(\text{C}_n\text{H}_{2n+1})$ , where  $n = 1$  to about 50;  
 $-\text{Ar}-\text{S}_2-\text{Ar}-\text{NH}_2$  and  $-\text{ArC}_p\text{H}_{2p}\text{Ar}-$ , where  $p = 1$  to about 10;  
 $-\text{Ar}-\text{S}_2-\text{Ar}-$  and  $-\text{ArC}_p\text{H}_{2p}\text{Ar}-$ , where  $p = 1$  to about 10; or  
 at least two different  $-\text{Ar}-\text{CO}_2(\text{C}_m\text{H}_{2m+1})$ , where  $m = 0$  to about 20.

The various organic, monomeric, and polymeric groups described above and below which are part of the modified particles can be unsubstituted or substituted and can be branched or linear.

As described earlier, one or more organic groups can be attached to the pigment.  
5 Further, two or more modified pigments, each having a different organic group attached to the pigment, can be used. Also, one organic group having an ionic or ionizable group can be used in connection with a second or additional organic groups with or without ionic or ionizable groups and so on.

In addition, the microscopic containers can contain particles having particles  
10 wherein a portion of the particles have one type of organic group attached onto the particles and another portion of the particles have a different organic group attached to the particles. The advantage of such a system would make it possible to have organic groups having ionic and/or ionizable groups such that their response to a potential difference is different. In other words, one organic group may have ionic and/or ionizable groups  
15 having a greater affinity for a positive or negative charge compared to other particles having a different organic group with an ionic and/or ionizable group. This type of situation may permit the ability to achieve multi-color displays with numerous options. In another embodiment, the microscopic containers can be different. In other words, a portion of the microscopic containers can contain one type of particles having an organic group  
20 with an ionic and/or ionizable group and another portion of microscopic containers can contain particles with a different type of organic group having an ionic and/ionizable group wherein the response to a potential difference between the different types of microscopic containers can be different again creating the ability to have a multi-color display.

The particles having the different types of organic groups as described above would  
25 preferably involve particles having different colors so that one particle would have one color while a second particle would have a different color as well as a different organic group having an ionic and/or ionizable group having a different response to a potential difference between the electrodes thus creating different electrophoretic mobilities which are preferably substantially non-overlapping in order to create various multi-colored displays. Thus, when  
30 the response to the potential difference differs amongst the various colored particles based on the type of organic group attached to each of these particles, controlling the electric field permits the desired display described in U.S. Patent No. 6,017,584 incorporated in its entirety

by reference herein. Unlike the '584 patent which is strictly dependent on the zeta potential of the particles themselves, the present invention can alter and/or create the desired zeta potential on the various particles in order to achieve the desired electrophoretic mobility of the various particles.

5        In addition, for purposes of the present invention, conventional particles (e.g., charged or uncharged) can be used in combination with the modified particles of the present invention to accomplish the desired multi-colored display.

10        The improvements described in various electrophoretic display systems can also be incorporated into the present invention such as using reflective components, placing a charge opposite in polarity to the particles on the inside walls of the microscopic containers, using liquid crystal materials whose orientation is affected by the electric field, and the like.

      Though not necessary, surface treatment agents and other conventional ingredients can be used in the present invention.

15        Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the present specification and practice of the present invention disclosed herein. It is intended that the present specification and examples be considered as exemplary only with a true scope and spirit of the invention being indicated by the following claims and equivalents thereof.

**WHAT IS CLAIMED IS:**

1. An electrophoretic displays comprising:
  - a) an arrangement of microscopic containers, wherein each container comprises a dielectric fluid and a suspension of particles having attached at least one organic group, wherein said organic group includes at least one ionic group, ionizable group, or both, wherein said fluid and said particles contrast visually;
  - b) first and second electrodes wherein said arrangement is located between said electrodes and wherein at least one of the electrodes is substantially visually transparent; and
  - c) means for creating a potential difference between the two electrodes, wherein said potential difference causes said particles to migrate towards one of the electrodes.
2. The electrophoretic display of claim 1, wherein said microscopic containers are discrete and are about 500 microns or less in dimension.
3. The electrophoretic display of claim 1, wherein said organic group is polymeric.
4. The electrophoretic display of claim 1, further comprising a pigment not having dual treatment attached an organic group.
5. A non-emissive display system comprising:
  - a) at least one display element located between two electrodes wherein the display element is visually responsive to a potential difference between the electrodes; and
  - b) a display piezoelectric element connected to the electrodes wherein deformation of the piezoelectric element produces the potential difference;wherein said display element comprises an arrangement of microscopic containers, wherein each container comprises a dielectric fluid and a suspension of particles having attached at least one organic group, wherein said organic group includes at least one ionic, ionizable group, or both, wherein said fluid and said particles contrast visually.
6. A multi-color electrophoretic display comprising at least two types of particles, wherein one type of particles having attached a first organic group having an ionic group, ionizable group, or both and another portion of particles having a second organic group having an ionic group, ionizable group, or both, wherein said particles have

substantially non-overlapping electrophoretic mobilities, and wherein the multi-color display permanently displays one of the types of particles in response to a sequence of electrical pulses controlled in both time and amplitude.

7. The electrophoretic display of claim 6, further comprising at least a third  
5 type of particles having a third organic group having an ionic group, ionizable group, or both which has a substantially non-overlapping electrophoretic mobility compared to the first and second type of particles.

8. A visual display device or display media comprising an arrangement of  
10 particles wherein an optical response results from movement of said particles in an electric fluid, wherein said particles have attached at least one organic group having an ionic group, ionizable group, or both.

9. The visual display device or display media of claim 8, wherein said particles rotate to create said optical response.

10. The visual display device or display media of claim 8, wherein said  
15 particles move vertically or horizontally or both to create said optical response.

11. The visual display device or display media of claim 8, further comprising a second organic group attached to said particles.

12. The visual display device or display media of claim 8, further comprising  
20 pigments having no attachment of organic groups.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/28189

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 G02F1/167

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G02F G09F G03G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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X	US 5 930 026 A (JACOBSON JOSEPH M ET AL) 27 July 1999 (1999-07-27) cited in the application column 2, line 13 - line 67 column 4, line 66 -column 5, line 56; figures 1A,3-4B	1-3,5,8, 10
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Y	US 6 017 584 A (ALBERT JONATHAN D ET AL) 25 January 2000 (2000-01-25) cited in the application column 2, line 33 -column 3, line 15 column 8, line 41 -column 9, line 5 column 12, line 45 -column 13, line 8; figures 5,9,10	9
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## ° Special categories of cited documents :

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- \* & \* document member of the same patent family

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## INTERNATIONAL SEARCH REPORT

I International Application No  
PCT/US 01/28189

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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